“Development of Efficient Nanoparticle Doped Zinc Oxide Photocatalysts for Degradation of Organic Dyes.”

A Synopsis

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Abstract:

The efficient remedy of organic dyes from wastewater is increasingly valuable in water treatment technology, due to the tons of hazardous chemicals presently and constantly released into rivers and seas from various industries, including the textile, paper, pharmaceutical, and dye production industries. Using solar energy as an inexhaustible source, photocatalysis ranks among the most promising industrial wastewater treatment techniques for eliminating persistent organic pollutants and new emerging contaminants. In that situation, developing efficient photocatalysts using sunlight irradiation and effectively integrating them into reactors, however, pose major challenges in the technologically relevant application of photocatalysts. As a potential solution, nanometal doped zinc oxide (ZnO) nanocomposites may be used together with different components (i.e., ZnO and TiO_2, SnO_2, MnO_2, Fe_2O_3 and Graphene oxide-based materials) to overcome the drawbacks of ZnOphotocatalysts. Indeed, mounting evidence suggests that using doped nanometalZnOnanocomposites can promote light absorption, charge separation, charge transportation, and photo-oxidation of dyes. Despite such advances, viable, low-cost metal doped ZnOnanocompositephotocatalysts with sufficient efficiency, stability, and photostability remain to be developed, especially ones that can be integrated into photocatalytic reactors. This research proposal is a brief overview of state-of-the-art metal doped ZnOnanocomposites and the mainadvantages and challenges in developing them.

Introduction:

Energy and environmental problems are the most pressing topical issues of our planet today (Umezawa& Ye, 2012). The two topics go in a cycle. Fossil fuels are the mainstay of most technologies in fashion currently, and their excessive use is also the primary reason for many of the environmental problems that are being encountered (Marschall& Wang, 2014). Jettisoning fossil fuels and shifting focus to renewable energy technologies are the apparent solution to this vicious circle (Jiang et al., 2017; Marschall& Wang, 2014).

Rapid industrialization as well as population growth in the past 50 years have made actions against water scarcity and water pollution urgent priorities for governments, industries, and civil society worldwide. The 2020 United Nations World Water Development Report estimated that nearly 748 million people are unaware of the shortage of pure water drinking and that the water required by manufacturing industries will increase by a staggering 400% by 2050 [1]. Each year, approximately 3.2 million people die, especially in developing countries, because they cannot access clean water or sufficiently sanitary environments [2]. Beyond that, several types of inorganic and organic compounds consumed in large amounts have become a dangerous factor in the devastation of the world's ecology. Against that background, more efficient processes for decontaminating water urgently need to be developed as conventional wastewater treatments become inefficient for remediating a range of persistent organic pollutants (e.g., pesticides, herbicides, dyes, and surfactants) and new emerging contaminants (e.g., trace organic compounds, nanoparticles, microplastics, cyanotoxins, and antibiotics). However, several limitations—the complexity and the time-consuming nature of the processes, the higher cost of operations and chemicals used, aggregate sludge production, and difficulties with separation—inhibit their potential use [3]. Against of all those limitations, advanced oxidation processes, based upon the catalytic or photocatalytic heterogeneous or homogeneous oxidation of complex organic pollutants are considered to rank among the best candidate technologies for efficient wastewater treatment. Among advanced oxidation processes, photocatalysis is possibly the most promising due to the simple, environmentally friendly conditions required, including the use of solar light as an energy source and, in turn, lower energy costs and less energy consumption. Heterogeneous photocatalysis could be efficient for mineralizing organic pollutants (i.e., total oxidation) and photo reducing toxic inorganic heavy metals such as hexavalent chromium [4,5]. The various scientific and technical barriers prevent the use of heterogeneous photocatalystsamong others, their inefficient integration into fixed reactors or the limited post- recovery of unfixed

photocatalysts after water treatment; the wide bandgap of potential photocatalysts, which restricts their use only under UV irradiation and, in turn, significantly increases costs, namely because solar light contains only 5% of UV light; and low durability and efficiency of photocatalytic treatment processes [6–8].

Since 1972, various metal oxides have been investigated as heterogeneous photocatalysts for wastewater treatment; examples include zinc oxide (ZnO), iron (III) oxide (Fe_2O_3), titanium dioxide (TiO_2), tungsten trioxide (WO_3), zirconia (ZrO_2), niobium pentoxide (Nb_2O_5), and vanadium oxide (V_2O_5) [9,10].

Among those semiconductors, ZnO has shown great potential in recent years due to its unique characteristics, including chemical stability, biocompatibility, a robust ability amid oxidation, acceptable photocatalytic performance, exceptional photosensitivity, good pyroelectric and piezoelectric properties due to its shape and size, and potentially simple synthesis using various scalable methods [11]. ZnO-nanoparticles are smaller than bulk materials and have a high specific surface area (i.e., high active sites), and both of those qualities facilitate the adsorption of pollutants and subsequent mineralization when irradiated with UV light due to the production of photogenerated charge carriers and reactive oxygen species (ROS) such as hydroxyl radicals. However, the relatively broad bandgap is approximately 3.37 eVrequires the use of UV light, the rapid recombination of electron-hole pairs, and low photo corrosion resistance, thus inhibiting their practical use.

Review of Literature:

A comprehensive review of literature on the principles of photocatalysis, different types of photocatalysts, structural properties and photocatalytic performance comparison between TiO2 and ZnO, synthesis methods of ZnONPs, discussion of main parameters that affect the photo efficiency and the development of devices for photocatalytic applications has been reviewed.Photocatalysis generally involves the process of photosensitization, where a photochemical reaction occurs in one chemical species due to the absorption of photonic energy by another species called photosensitizer [12].

B. Cao et al, discussed incoming photons with energies larger than the band gap energy (ΔE) of the photocatalyst are absorbed, the electrons in the valence band (VB) of the semiconductor photocatalyst are excited into the conduction band (CB), leaving behind an equal number of holes in the VB [13].

K. Pirkanniemi and M. Sillanpää, In the history of heterogeneous photocatalysis, a lot of noble metals, such as Pt, Pd, Ru, Ir and Rh, and some metal oxides, such as Ti, Zn, W, Cu, Mn, Cr and Co, have been used as photocatalysts [14].

Z. L. Wang, In the past few decades, a large variety of “bottom-up” techniques have been employed to generate 1D nanostructures.ZnO nanostructures synthesized under different controlled conditions (reproduced from [15].

Y. C. Kong et al,the final shape and aspect ratio of the resultant ZnO nanostructures are dependent on the relative growth rates on the different crystalline faces.The vapor phase synthesis is the most extensively used approach to synthesis 1D nanostructures. Many research groups, such as Kong et al[16], Yao et al[17] and Zhang et al[18] have used this technique to fabricate ZnOnanorods or nanowires with high quality, single-crystalline.

E. W. Petersen, the most common vapor synthesis methods include vapor liquid solid (VLS) growth [19], physical vapor deposition (PVD),L. Wang et al [20], chemical vapor deposition (CVD), L. N. Protasova etal [21], metal organic chemical vapor deposition (MOCVD) S. Ashraf etal[22], molecular beam epitaxy(MBE), J. S. Wang [23], pulsed laser deposition (PLD), L. C. Tien et al [24], and so on.Since first developed by Wagner and Ellis in the 1960s to fabricate micrometre-sized whiskers [25], the solution phase synthesis has been reported to be advantageous due to its low growth temperature, low cost, ease of handling and potential scalability for producing high-density arrays. The synthesis process can take place in either aqueous, B. Liu and H. C. Zeng etal [26] or organic solutions, C. Wu et al [27] or even a mixture of the two, S. K. Lim et al [28].

M. Afifi et al, Nanoparticle synthesis is mediated by physical, chemical and green methods [29] [30] [31].

R. Chandrasekaran et al, the physical method involves the use of costly equipment, high temperature and pressure [32], large space area for setting up of machines. The chemical method involves the use of toxic chemicals which can prove to be hazardous for the environment and the person handling it.

P. Dhandapani et al, the literature states that some of the toxic chemicals that we use in physical and chemical methods may reside in the NPs formed which may prove hazardous in the field of their application in the medical field [33]https://www.sciencedirect.com/science/article/pii/S2405653717300283 - bib0080.

SandeshJaybhaye et al, discussed there isneed an environment-friendly and cost-effective method for nanoparticle synthesis [34-37].

Y. Zhang et al, in recent years, since doping of semiconductors with metal and/or transition metals increases surface defects, and enhance their optical absorption and shift into visible light regime (400-800nm). The semiconductors, such as TiO_2, ZnO, WO_3, Fe_2O_3 and ZnS, have drawn increasing interest as effective photocatalysts in the photocatalytic process, due to their higher stability than metals and higher electrical conductivity than insulators [38].

S. Baruah et al,reported that ZnOnanostructures doped with silver (Ag) [39], lead (Pb) [40], cobalt (Co) [41] and manganese (Mn) [42] have shown enhanced visible light absorption and photocatalytic activity.

A. Fujishima et al, In the past few decades, TiO2 has been widely used as one of the most efficient photocatalysts for many environmental applications [43], since the discovery of using TiO2 photoanode for successful photolysis of water under UV light with a wavelength smaller than 190nm by Fujishima*et al* in 1972 [44].

A. Sapkota et al, ZnO has been increasingly recognized as a suitable alternative to TiO2, as its band gap energy is comparable with that of TiO2 and its photocatalytic degradation mechanism has been proven to be similar to that of TiO2 [45].

In fact, ZnO has been reported to be more efficient than TiO2 in some cases, for instance, in the advanced oxidation of pulp mill bleaching wastewater [46], and photocatalyzed degradation of phenol [47].

M. Yeber et al, In the field of dye-sensitized solar cells (DSSCs), ZnO-based DSSC techniques are also preferred than TiO_2-based ones due to a faster electron transport rate in ZnO with a reduced recombination rate, and its ease of crystallization and anisotropic growth [48].

B. Cao et al, to date, several strategies have been used to improve the performance of ZnO, including ion doping, composite, metal loading, coupling it with semiconductors, structural design improvements, and combining it with carbon materials, [49].

F. Lu et al, among carbon-based materials, graphene oxide (GO) is an ideal candidate for integration with ZnO-based photocatalysts, due to not only its outstanding dispersive ability inside any solvent [50].

S. Ahmed et al, recently, the use of GO-based ZnOnanomaterials for photocatalytic applications has become more popular due to their excellent physicochemical and photo-electrochemical properties [51-53].

This Research focuses on the synthesis of ZnO nanoparticles by bio reduction method, doping with tin and Titanium dioxide and their significant role in the photodegradation of

organic dyes. The proper photocatalytic degradation mechanism of dyes, and several factors of dye degradationwill be analysed.

Aims and Objectives:

Aim: The main aim of the present work is the preparation of eco-friendly ZnO nanostructured materials by bio-reduction with ordered structure and study of its photocatalystapplication potential.

Objectives of the study:

1. To prepare the nanostructured material by chosen/knownBio reduction methodswith respect to desired structure and morphology of the ZnO NPs.
2. To investigate the effects of Fruits extract, pH, Ultrasonication, temperature and concentration of Metal salt solutions, and the growth time of theZnO NPs.
3. Characterization of morphology, structure, optical, surface and other properties of the prepared powdered materials.
4. To evaluate the reproducibility of the experimental methods used, and to test the reusability of the prepared ZnO NPs as photocatalysts for multiple cycles.
5. To fabricate the macro-chamber-basedphotocatalytic property measurement device integrated with ZnO NPs, and measure its photo efficiency with the conventional methods.
6. To investigate the effects of chamber height, concentration, time, type of dyes, and flow rate on the photocatalyticefficiency of organic dyes degradation.
7. To prepare a composite system with Tin oxide, Titanium dioxideand CNTs-basedZnOnanocomposites for the photo-oxidation of organic dyes.
8. Analysis of the obtained composite properties, in terms of photocatalystand effects on organic dyes degradation using dyes industry effluent.

Materials and Methods:

Reagents and Chemicals

Zinc nitrate hexahydrate, titanium tetra chloride, ethanol, Sodium Hydroxide, Hydrochloric acid,methyleneblue trihydrate (MB) will be purchased from S D Fine-Chem Limited, Mumbai, India. All the chemicals will be used as received. We will make use ofMultiwalled Carbon nanotubes taken from Nanotech Research Lab, Birla College, Kalyan obtained by Dr.SandeshJaybhaye using Acetylene gas by Chemical Vapour Deposition Method.Deionised double distilled water will be used for synthesis of plant extracts. Plant extract will be prepared from the fruits collected from the Ulhasnagar fruit market (nearR.K. Talreja College, Ulhasnagar), Ulhasnagar, Maharashtra, India.

Methods:

Selections and preparation of Fruits Extracts

First, the pulp, seed, and skin parts of orange, grapes, pineapple fruits (contains lots of resveratrol, a phytochemical and antioxidant) were separated and subjected to boiling water digestion, grinding, and filtration. In all the methods, these parts were processed with 100 mL of D.I. water. For water digestion, these parts were separately treated at 100°C for 3 h and filtered. A kitchen grinder was used for grinding. The grounded contents digested in water were filtered with a 70 mesh streel filter.

Synthesis of Zinc Oxide nanoparticle

In this work, the molar ratio of plant extract and Metal Salts fixed i.e. 1:1 and the pH of the plant extract was adjusted by using 0.1 M HCl and NaOH solution. The pH of plant extract solution was 5, 7, and 9. In addition, the concentration of metal salts varied from 5mM, 10mM, 15mM with sonication time 60, 90, 120 min respectively.

Fabrication of ZnO-TiO_2 Composite

Synthesis of ZnO-TiO_2 nanocomposites using fruit peel extract. Fruit peels extract will be mixed with $Zn(NO_3)_2 \cdot 6H_2O$ and 1 wt % $TiCl_4$ will be taken in borosil glass container. After adding 10 mL deionized water, the solution was stirred for 10 min on a hot plate at 70°C. The resulting solution was centrifuged, washed with DI water and dried at 50 °C. The as-prepared product was further heated in air in a muffle furnace at 500 °C for 10 min to obtain ZnO –

TiO_2 nanocomposites. In the similar manner other composites namely 2% TiO_2–ZnO , 5% TiO_2–ZnO , and 10% TiO_2–ZnOnanocomposites can be obtained

Fabrication of ZnO-TiO_2- Carbon nanotubes Composite

Synthesis of ZnO-TiO_2-MWCNTsnanocomposites using fruit peels extract. Fruit peels extract was mixed with $Zn(NO_3)_2 \cdot 6H_2O$ and 1 wt % $TiCl_4$ and Functionalized MWCNTs will be taken in borosil glass container. After adding 10 mL deionized water, the solution was Refluxed for 30 min on a hot plate at 80°C. The resulting solution will be centrifuged, washed with DI water and dried at 50°C. The as-prepared product was further heated in air in a muffle furnace at 500°C for 10 min to obtain ZnO-TiO_2-MWCNTsnanocomposites.

Photocatalytic activity Measurement

As obtained ZnO nanoparticles, TiO_2–ZnOnanocomposites and ZnO-TiO_2-MWCNTsnanocomposites will be characterized in terms of their morphological, structural and optical properties, and will be used as photocatalysts for the degradation of toxic MB dye using fabricated Photocatalytic reactor.

Importance of the Study:

International status

This is an area of research which is carried out through-out the world unlike other areas of science. Research in particular areas of science is confined to ascertain regions of the world, but the degradation of dyes has been studied in almost all the countries and regions including almost all the developing countries around the world.Green nanotechnology has been defined as the development of clean technology which proactively affects the design of nanomaterials and products by decreasing or eliminating pollution from the fabrication of the nano-scale materials [54]. It has drawn on a framework of the principles of green chemistry and green engineering to enhance the environmental sustainability of nanomaterial products. This methodology triggers clean production processes such as natural sources which lead to green manufacture of nanoparticles for environmental remediation, renewable energy, water treatment, hazardous chemical substitution, and waste management applications.

Virtually, a great amount of ZnO NPs is effectively produced using traditional chemical and physical methods. Despite the advantage of these processes in the aspect of large-scale productions of nanomaterials using chemical methods, their adverse environmental impact is

a global concern [55].Thecurrent global colorant marketis 32 billion USD and is estimated to increase to 42 billion USDby 2021[56].

These nanoparticles demonstrate anti-corrosive, antifungal, photochemical, catalytic, electrical, antibacterial, UV filtering, and photovoltaic properties.Accordingly, there is a crucial need to develop sustain-able and eco-friendly techniques for producing green NPs [57]. A considerable number of green approaches using natural sources such as microorganisms and plant extracts for zinc nanoparticle synthesis has been suggested a promising alternative to chemical methods [58,59].

National Status:

Recently, water contamination by dye discharges from variousindustries (e.g., paper making, textile dyeing, cosmetics, paints, food processing, etc.) has attracted significant attention due to hazards to public health and ecosystems [60]. The annual total production of synthetic dyes is over 700,000 tons. Strong economic growth with the rapid urbanization of cities has resulted in an exponential rise in drinking water demand and wastewater generation. The per capita wastewater generated by the Indian cities and towns, representing more than 70% of urban population in India. The metro cities like Mumbai and Delhi, the rate is a day by day became worst. An alarmingly high 70% of the urban wastewater flows untreated into the river and sea.This work will help provide a better understanding of photocatalysis for dye degradation in industrial waste water in India andhighlight the current challenges forcommercializing the process.Photocatalytic degradation of dyes or other organic pollutants is an intensively pursued research exercise mainly from the last quarter half of the 20^{th} century [61].

Nowadays, thesynthetic dyes are extensively usedin products like clothes, leather accessories, furniture, and plastic products. However, during the dyeing process, nearly 12% of these dyes exclude as waste,and ~ 20% of this wastage enters to the environment [62].

To expand the photocatalyst applications toindustrial scale, the post separation problems associated with the first- and second-generation materials were addressed by the third generation nanomaterials based photocatalysts. The third generation photocatalysts are smart (e.g., due to larger surface area and greater reaction sites) presented a new opportunity to develop or improve immobilization technologies. The limitations and challenges that currently undermine the industrial applications of photocatalysts can be resolved in India. In conclusion, the Nanomaterials materials hold a tremendous potential for the future of dye wastewater treatment on an industrial scale.

Different nanoparticles of ZnO nanoparticles, TiO_2–ZnOnanocomposites and ZnO-TiO_2-MWCNTsnanocomposites were successfully synthesized through environmentally friendly novel green method using fruit peel waste. The as-synthesized ZnO-TiO_2-MWCNTsnanocomposites possess maximum catalytic activity (~96%) to degrade the MB dye within 80 min by visible light, which demonstrates the potential application towards the wastewater purification with environmentally friendly material. These photocatalysts can be applied as fruitful photocatalytic material on industrial scale for the exploitation of structurally stable and complex dyestuff. This study offers a green and non-toxic method containing biomaterials to synthesize various nanomaterials using this eco-friendly preparation route.

Proposal work plan:

Preparing time schedule and strictly adhering to it, would complete the study efficiently with satisfaction. Due flexibility must be kept in the schedule so that if there are some unforeseen difficulties those can be overcome or by passed by taking proper guidance and consultation with the expert in the field.

1.	March 2022-August 2022	:	Study of related literature, Bibliographical Search, writing of research proposal, survey of samplings.
2.	August 2022- January 2023	:	Synthesis of the nanostructured material by Bio reduction methods of the ZnO nanoparticles. Study the effects of fruit extract, pH, sonication, temperature and concentration of MO solutions, and the growth time of the synthesis ZnO NPs.
3.	January2023-June 2023	:	Characterization of morphology, structure, optical, surface and other properties of the powdered nanomaterials. Evaluate the reproducibility of the experimental methods used, and to test the reusability of the prepared ZnO nanoparticles as photocatalysts for multiple cycles.
4.	June 2023-November 2023	:	Fabrication of the macro-chamber-based device integrated with ZnONPs, and measure its photo efficiency with the conventional methods. Investigate the effects of chamber height, concentration, time, dyes, and flow rate on the photocatalytic efficiency of dyes degradation applications.
5.	November2023-April 2024	:	Preparation of a composite with Tin oxide, Titanium

			dioxide and CNTs-based ZnOnanocomposites for the photo-oxidation of organic dyes. Analysis of the composite properties, in terms of photocatalyst and effects on organic dyes degradation.
6.	April 2024- September 2024	:	Thesis submission

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